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(19)

(54) REMOVING METALS FROM SULPHIDE ORES

(71) We, CYPRUS METALLURGICAL PROCESSES CORPORATION, a Corporation organised and existing under the laws of the State of Colorado, United States of America, of 555 South Flower Stree, Los Angeles, California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to processes for recovering metals from sulphide ores containing lead, silver and zinc sulphides.

It has been proposed hitherto to convert metallic sulphides into chlorides in metal recovery processes. For example metal sulphide concentrates can be chlorinated with ferric chloride and chlorine gas in aqueous sodium chloride or calcium chloride, (see U.S. Patent 1,736,659).

It has also been proposed hitherto ("The Dry Chlorination of Complex Ores" by Ionides in Mining and Scientific Press, Volume 112, May 27, 1916), to chlorinate dry concentrates of metal sulphides containing lead, zinc and silver sulphides, using chlorine gas. A final chlorination is effected in a roasting step in the presence of air, ferric chloride formed in the chlorination step being decomposed to produce chlorine which completes the chlorination of the metal sulphides. This latter hitherto proposed process can be used for the production of zinc chloride, and it is not a pollution-free process as sulphur dioxide is produced in the roasting step and it is released into the atmosphere. Furthermore, when the chlorination product is treated with sodium chloride to solubilize the metal chlorides, an undesirable build-up of impurities, particularly zinc chloride, occurs in the brine leach solution. This adversely affects the ability of the solution after a period of time to solubilize silver and lead chlorides from the chlorinated ore product.

According to one aspect of the present invention there is provided a process for recovering metal values from a sulphide ore concentrate containing lead, silver and zinc sulphides, the process comprising the steps of:

(a) chlorinating the concentrate to convert the metal sulphides into metal chlorides and to convert sulphide sulphur into elemental sulphur;

(b) leaching the non gaseous product from step (a) with aqueous sodium chloride to dissolve lead and silver chlorides therein therby to enable separation of these chlorides from insoluble solids;

(c) cooling the sodium chloride leach solution to precipitate substantially all of the lead chloride therein followed by separating the precipitated lead chloride from the leach solution;

(d) recovering silver from the lead chloride-depleted leach solution obtained in step (c);

(e) removing a portion of the solution produced in step (d) and passing the remainder of the solution to the leach solution of step (b);

(f) removing substantially all of the zinc and other impurities from the portion of solution removed in step (e);

(g) part electrolysing the removed portion of the solution to produce chlorine gas while leaving a weakened sodium chloride solution;

(h) passing the remaining electrolyte solution to step (b); and

(i) passing chlorine gas produce in step (g) to step (a).

According to another aspect of the present invention there is provided a

process for recovering metal values from a galena/tetrahedrite ore concentrate containing lead, silver, antimony and zinc sulphides, the process comprising the steps of:

(a) dry chlorinating the pulverized concentrate with chlorine gas at a temperature of from 50 to 150°C to convert the sulphides into chlorides, to volatilize antimony chloride produced, and to convert the sulphide sulphur into elemental sulphur;

(b) leaching the non gaseous product from step (a) at a temperature of from 80 to 100°C with an aqueous solution containing from 250 to 300 grams/litre of sodium chloride to dissolve lead chloride and silver chloride, and to extract these chlorides from the remaining solids;

(c) cooling the sodium chloride leach solution from step (b) to about 20°C to precipitate substantially all of the lead chloride and separating the precipitated lead chloride therefrom;

(d) fusing the lead chloride from step (c) and electrolyzing the fused salt to produce chlorine gas and lead;

(e) passing the chlorine gas from step (d) to step (a);

(f) recovering silver from the lead chloride-depleted leach solution remaining from step (c) by cementation with metallic iron;

(g) removing from 5 to 15% by weight of the silver and lead-depleted leach solution from step (f), and passing the remainder of the depleted leach solution to the leach solution of step (b);

(h) removing any lead and silver remaining in the removed portion of the metal-depleted solution by iron cementation;

(i) precipitating zinc and other impurities from said removed portion of the metal-depleted solution using sodium carbonate;

(j) part electrolysing sodium chloride in said removed portion of the metal-depleted solution to produce chlorine gas while leaving a weakened sodium chloride solution;

(k) passing the chlorine gas from step (j) to step (a);

(l) carbonating sodium hydroxide formed in step (j) to produce sodium carbonate and passing the sodium carbonate to step (i); and

(m) passing the remaining sodium chloride solution from step (j) to step (b).

According to a further aspect of the present invention there is provided a process for recovering metals from an ore containing lead, silver, and zinc sulphides, the process comprising chlorinating the sulphide ore to produce the chlorides of the metals and liberate elemental sulphur, leaching the chlorides with sodium chloride to remove lead and silver chlorides, separating lead chloride from silver chloride by cooling the leach solution, recovering silver by cementation of the lead chloride-depleted solution, reducing the concentration of zinc and other impurities in a portion of the lead and silver-depleted leach solution, and passing both the zinc-depleted and non zinc-depleted portions of the lead and silver depleted leach solution to the leaching step.

According to a yet further aspect of the present invention there is provided a process for recovering metals from a sulphide ore containing at least the sulphides of lead, silver, and zinc, the process comprising converting the sulphides into chlorides by chlorination, leaching the chlorides into sodium chloride solution, removing lead chloride from the leach solution by crystallization for the recovering of lead, recovering silver from the leach solution by cementation, removing zinc from a portion of the resulting lead and silver-depleted solution as zinc carbonate, returning the untreated portion of the lead and silver-depleted solution to the leaching step, electrolyzing the zinc-depleted solution containing sodium chloride to produce chlorine, the chlorination step being effected using dry chlorine gas to convert the metal sulphides to chlorides and sulphide sulphur to elemental sulphur.

Using a process employing the present invention, sulphide ore concentrates containing lead, silver and zinc sulphides can be treated in particular to recover silver and lead. The recovery of metals from their chlorides resulting from the chlorination step is effected so as to prevent the build-up of impurities, including zinc chloride, in the sodium chloride leach solution used to solubilize the metal chlorides formed in the chlorination step. As an alternative to wet chlorination of the sulphides, dry chlorination can be effected using dry chlorine gas, with heating to convert the sulphides to chlorides and to volatilize the chlorides of arsenic and antimony, if these metals are present. Dry chlorination has been found particularly effective with sulphides of the tetrahedrite-tennantite series either alone or

combined with some other mineral such as galena.

After chlorination of the sulphides by any method, metal chlorides are leached into warm sodium chloride solution and separated from the resulting solution. The metals, lead and silver, which are of principal interest are then recovered from the separated aqueous chlorides. Lead chloride is crystallized by cooling, and lead can be recovered from the lead chloride by fused salt electrolysis with the chlorine produced being passed to the chlorination step. Silver can be removed from the lead chloride-depleted solution by cementation. The resulting lead and silver-depleted solution, from which a portion has been separated, is passed to the sodium chloride brine leach. The separated portion of the metal-depleted solution, after removal of lead and silver therefrom by iron cementation, is preferably neutralized with sodium carbonate to remove zinc and other metal impurities as carbonates. Part electrolysis of the resulting solution produces chlorine which is passed to the ore chlorination step while some of the weak sodium chloride electrolyte remaining is concentrated and passed to the sodium chloride brine leach to prevent the build-up of zinc and other impurities when the process is being effected continuously. Sodium hydroxide from the electrolysis is preferably carbonated and the resulting sodium carbonate used in the neutralization step.

The recycling to the initial sodium chloride leaching solution of a portion of the lead and silver chloride depleted sodium chloride leach solution after the removal of zinc and other metal impurities enables zinc chloride to be removed from the brine leach solution at substantially the same rate that it is added thereto by the ore. This can prevent its build-up in the brine leach solution, which would otherwise inhibit the solubilization of lead chloride. In addition, chlorine is retained in the system, so that substantially no chlorine leaves the system as chloride in impurities or otherwise. Any chlorine which is removed is removed as chlorine gas in the electrolysis and it is passed to the chlorination step without substantial loss of chlorine. The present invention provides a substantially pollution-free process, with no chlorine or lead vapours or compounds being released into the atmosphere. Substantially all of the sulphide sulphur is converted into elemental sulphur rather than sulphur dioxide, unlike pyrometallurgical processes.

A process employing the present invention will now be described, by way of example, with reference to the accompanying diagrammatic drawings in which:—

Figure 1 is a flow diagram showing the various steps in the exemplified process; and

Figure 2 is a flow diagram showing chlorination of a concentrate containing lead, silver, zinc and antimony in a kiln.

The concentrate was a galena/tetrahedrite concentrate having the following analysis:—

Silver	0.30— 0.35%
Lead	68 —70%
Antimony	0.80— 1.4%
Sulphur (Total)	14 —17%
Zinc	4 — 6%
Iron	2 — 4%

It is to be understood that other ores containing sulphides of lead, silver and zinc can be treated. The reactions occurring in the chlorination step are:

$$MS = Cl_2 \rightarrow MCl_2; \text{ (M = Pb, Zn, Cu, Fe, or Ag, etc.)}$$

$$S_2 + Cl_2 \rightarrow S_2Cl_2$$

$$MS + S_2Cl_2 \rightarrow MCl_2 + 3/2\ S_2$$

$$Sb_2S_2 + 5\ Cl_2 \rightarrow 2\ SbCl_5 + 3/2\ S_2$$

EXAMPLE — Continued

Zone 2 Reaction:	Inert Gas	Nitrogen
	Temperature	110—115°C
	Time	1.5 Hr.
Leach Conditions:	Pulp Density	50 g Chlorinated Product per litre of Leach Solution
	Leach Solution	290 g/l NaCl, pH 1.5
	Temperature	95°C
	Time	1.5 to 3 Hrs.

Results:

	Assay, %		
	PbS Concentrate 100 g	Chlorinated Product 121 g	Leached Residue 18.6 g
Ag	0.34	0.28	0.012
Pb	70	58	0.12
Sb	1.2	0.41	0.098
Zn	4.5	3.7	16
Fe	2.7	2.3	7.9
Cu	0.94	0.80	0.18
Cl	<0.1	23	

% Sb Volatilized During Chlorination = 59

% Extracted During NaCl Leach—Ag = 99.3

Pb = 99.9

Sb = 96

Zn = 33

Fe = 47

Cu = 97

These results show that more than 99 percent of the lead and silver present in the concentrate were converted into the chloride and extracted during the brine leach. In addition a substantial amount of the antimony was recovered. Substantially all of the sulphide sulphur was converted into elemental sulphur in the dry chlorination step.

Using dry chlorination at a low temperature (80° to 115°C) with controlled chlorine addition (260—280 kg. of chlorine per metric ton of concentrate), followed by a sodium chloride leach at 90 to 95°C for an hour, 99% of the silver, 99.9% of the lead, 33% of the zinc, 47% of the iron, 97% of the copper and 96% of the antimony were extracted. During the chlorination, antimony was volatilized, probably as $SbCl_3$, and recovered from the waste gases. Arsenic, when present, can also be recovered in this manner. Substantially all of the sulphide sulphur in the metal sulphides was converted into elemental sulphur, unlike pyrometallurgical processes in which sulphur is released as the pollutant sulphur dioxide.

Referring to the flow sheet shown in Fig. 1, leaching described hereinbefore in the Example can be performed as follows. Irrespective of whether dry or wet chlorination is used, the flow sheet of Fig. 1 can be followed beyond the chlorination step. The chlorinated product is leached in the brine leach with sodium chloride solution to solubilize lead and silver chlorides, and other metal chlorides which act as impurities. After start-up, the brine leach solution is supplemented with recycled sodium chloride in a continuous process, as shown. The leach solution for the tetrahedrite/galena concentrate during operation ordinarily contains from 260 to 280 grams per litre of sodium chloride, approximately 40 grams per litre of lead, about 0.15 grams per litre of silver, 15 to 30 grams per litre of zinc, 15 to 30 grams per litre of ferrous iron, and lesser amounts of copper, antimony, calcium, magnesium, manganese, aluminium, etc. The brine leach step, irrespective of the concentrate being processed, is preferably performed at a temperature of from 80 to 100°C. The leach slurry is filtered hot, and the residue discarded or if desired processed to recover elemental sulphur.

The recovery of lead then follows. Solubilized lead chloride is crystallized from the sodium chloride leach solution by cooling from a temperature of 80 to 100°C to approximately 15 to 20°C. The resulting crystalline lead chloride is separated from the solution, for example by centrifuging, dried, and electrolyzed in a fused salt cell to produce product lead, and chlorine gas which is recycled to the chlorination step.

Silver can then be recovered by cementation from the lead chloride-depleted sodium chloride leach solution using metallic iron or lead to produce an impure silver sponge containing some copper, lead, iron and other trace impurities. Pure silver can be produced by refining this sponge. The lead and silver-depleted leach solution produced, minus a portion thereof, is passed to brine leach as shown.

About 5 to 15% of the metal-depleted leach solution is treated to remove impurities therefrom, especially zinc chloride, and the resulting impurity-depleted solution is fed to the brine leach. This enables the concentration of zinc chloride and other impurities in the leach solution to be controlled, since zinc chloride appreciably decreases the solubility of lead chloride in sodium chloride solutions. Accordingly, in order to dissolve large amounts of lead chloride, zinc chloride and other impurities are preferably removed from a portion of the metal-depleted leach solution at substantially the same rate as they are introduced in the chlorination step.

Treatment of a portion of the metal-depleted solution also enables impurities to be removed in a form other than as chlorides, which would otherwise result in a loss of chlorine from the system. Chlorine is recovered as a gas and it is passed to the chlorination step, thereby avoiding loss of chlorine from the system.

As shown in Fig. 1 lead remaining in the portion of the metal-depleted solution is removed by cementation with metallic iron, and the resultant sponge lead is recycled to the silver cementation step. Any silver cemented out will also be recycled, and the lead concentration in solution in said portion of the solution decreased from about 15 grams to 0.2 grams per litre.

The said separated portion of the solution is then neutralized with sodium carbonate at a pH of about 8.5 and at a temperature of 50 to 80°C to precipitate zinc, iron and other metal impurities in a readily filterable form as carbonates. Sodium carbonate is used because it reacts with zinc chloride to produce sodium chloride, which is subsequently electrolysed so that no chlorine is lost from the system in removing zinc and other impurities.

The bleed solution, after solids removal, is part electrolysed to produce chlorine gas, hydrogen gas, sodium hydroxide, and a weak sodium chloride solution. The prior removal of zinc and other impurities from the solution greatly facilitates the electrolysis, as the electrolysis is almost physically impossible if zinc and the other impurities are present in the electrolyte. The sodium hydroxide is carbonated to produce sodium carbonate which is recycled to the neutralization

step. The chlorine gas is passed to the chlorination step, and the impurity-depleted sodium chloride solution is concentrated and passed to the leach step to prevent zinc build-up in the leach solution.

Processes employing the present invention can, of course, be performed either continuously or batch-wise.

Based on the results obtained using dry chlorination, a material balance for a typical commercially available lead sulphide concentrate (galena/tetrahedrite) is as follows:

ESTIMATED MATERIAL BALANCE FOR GALENA/TETRAHEDRITE.

Kg/metric Ton of Concentrate

	Ag	Pb	Sb	Zn	Fe	Cu	S
Input							
PbS Concentrates	3.00	618	10.6	39.7	23.7	8.3	140
Iron Powder					16		
	3.00	618	10.6	39.7	39.7	8.3	140
Products							
Lead		611.4					
Ag Sponge	2.96	2.2	4.0		2.2	7.9	
Sb Chloride			6.2				~4
Leach Residue	0.04	3.5	0.4	26.5	12.8	0.4	~136
Impurities Carbonates		0.9		13.2	24.7		
	3.00	618	10.6	39.7	39.7	8.3	140

All the chlorine gas added was used internally.

This Table shows that in theory all of the lead and silver can be recovered without chlorine being lost from the system. After start-up, virtually no chloride has to be added to a continuously operated process, subject to losses resulting for example from mechanical operations, such as filtration, concentrations, etc.

While the invention has been illustrated in relation to treating a tetrahedrite/galena concentrate containing lead, silver and zinc and the use of a dry chlorination procedure, it is not limited to treating this ore or to using dry chlorination. Thus dry or wet chlorination can be used on ores in general containing lead, zinc and silver. The flow sheet of Fig. 1 can then be followed beyond the chlorination step, irrespective of the method of chlorination. Furthermore, metals can be recovered from their chlorides which have been produced by wet chlorination of their sulphides, and results comparable to those obtained in the Example hereinbefore can be achieved.

WHAT WE CLAIM IS:—

1. A process for recovering metal values from a sulphide ore concentrate containing lead, silver and zinc sulphides, the process comprising the steps of:

(a) chlorinating the concentrate to convert the metal sulphides into metal chlorides and to convert sulphide sulphur into elemental sulphur;

(b) leaching the non gaseous product from step (a) with aqueous sodium chloride to dissolve lead and silver chlorides therein thereby to enable separation of these chlorides from insoluble solids;

(c) cooling the sodium chloride leach solution to precipitate substantially all of the lead chloride therein followed by separating the precipitated lead chloride from the leach solution;

(d) recovering silver from the lead chloride-depleted leach solution obtained in step (c);

(e) removing a portion of the solution produced in step (d) and passing the remainder of the solution to the leach solution of step (b);

(f) removing substantially all of the zinc and other impurities from the portion of solution removed in step (e);

(g) part electrolysing the removed portion of the solution to produce chlorine gas while leaving a weakened sodium chloride solution;

(h) passing the remaining electrolyte solution to step (b); and

(i) passing chlorine gas produced in step (g) to step (a).

2. A process as claimed in claim 1, performed continuously.

3. A process as claimed in claim 1 or claim 2, in which lead and silver remaining in the said portion removed in step (e) are removed by iron cementation before zinc is removed in step (f).

4. A process as claimed in any of the preceding claims, in which zinc is removed from said portion in step (f) by neutralization with sodium carbonate to form sodium chloride and zinc carbonate.

5. A process as claimed in claim 4, in which sodium hydroxide formed in the electrolysis of the sodium chloride in step (g) is carbonated to form sodium carbonate which is used to effect the neutralization.

6. A process as claimed in any of the preceding claims, in which said portion removed in step (h) is concentrated before being passed to step (b).

7. A process as claimed in any of the preceding claims, in which the concentrate is chlorinated in step (a) using dry chlorination with dry chlorine gas.

8. A process as claimed in claim 7, in which the dry chlorination is effected at a temperature below the melting point of elemental sulphur.

9. A process as claimed in claim 7, in which the dry chlorination is effected at a temperature of 50 to 150°C.

10. A process as claimed in any of the preceding claims, in which the sodium chloride leach solution contains from 250 to 300 grams per litre of sodium chloride.

11. A process as claimed in any of the preceding claims, in which step (b) is effected at a temperature of 80 to 100°C.

12. A process as claimed in any of the preceding claims, in which the sodium chloride leach solution from step (c) is cooled to about 20°C to precipitate lead chloride.

13. A process as claimed in any of the preceding claims, in which silver is recovered in step (d) by cementation with metallic iron.

14. A process as claimed in any of the preceding claims, in which the concentrate is a galena/tetrahedrite ore.

15. A process for recovering metal values from a galena/tetrahedrite ore concentrate containing lead, silver, antimony and zinc sulphides, the process comprising the steps of:

(a) dry chlorinating the pulverized concentrate with chlorine gas at a temperature of from 50 to 150°C to convert the sulphides into chlorides, to volatilize antimony chloride produced, and to convert the sulphide sulphur into elemental sulphur;

(b) leaching the non gaseous product from step (a) at a temperature of from 80 to 100°C with an aqueous solution containing from 250 to 300 grams/litre of sodium chloride to dissolve lead chloride and silver chloride, and to extract these chlorides from the remaining solids;

(c) cooling the sodium chloride leach solution from step (b) to about 20°C to precipitate substantially all of the lead chloride and separating the precipitated lead chloride therefrom;

(d) fusing the lead chloride from step (c) and electrolyzing the fused salt to produce chlorine gas and lead;

(e) passing the chlorine gas from step (d) to step (a);

(f) recovering silver from the lead chloride-depleted leach solution remaining from step (c) by cementation with metallic iron;

(g) removing from 5 to 15% by weight of the silver and lead-depleted leach solution from step (f), and passing the remainder of the depleted leach solution to the leach solution of step (b);

(h) removing any lead and silver remaining in the removed portion of the metal-depleted solution by iron cementation;

(i) precipitating zinc and other impurities from said removed portion of the

metal-depleted solution using sodium carbonate;

(j) part electrolysing sodium chloride in said removed portion of the metal-depleted solution to produce chlorine gas while leaving a weakened sodium chloride solution;

(k) passing the chlorine gas from step (j) to step (a);

(l) carbonating sodium hydroxide formed in step (j) to produce sodium carbonate and passing the sodium carbonate to step (i); and

(m) passing the remaining sodium chloride solution from step (j) to step (b).

16. A process as claimed in claim 15, in which the concentrate includes arsenic sulphide and arsenic is volatilized in step (a).

17. A process for recovering metals from an ore containing lead, silver, and zinc sulphides, the process comprising chlorinating the sulphide ore to produce the chlorides of the metals and liberate elemental sulphur, leaching the chlorides with sodium chloride to remove lead and silver chlorides, separating lead chloride from silver chloride by cooling the leach solution, recovering silver by cementation of the lead chloride-depleted solution, reducing the concentration of zinc and other impurities in a portion of the lead and silver-depleted leach solution, and passing both the zinc-depleted and non zinc-depleted portions of the lead and silver depleted leach solution to the leaching step.

18. A process for recovering metals from a sulphide ore containing at least the sulphides of lead, silver, and zinc, the process comprising converting the sulphides into chlorides by chlorination, leaching the chlorides into sodium chloride solution, removing lead chloride from the leach solution by crystallization for the recovery of lead, recovering silver from the leach solution by cementation, removing zinc from a portion of the resulting lead and silver-depleted solution as zinc carbonate, returning the untreated portion of the lead and silver-depleted solution to the leaching step, electrolysing the zinc-depleted solution containing sodium chloride to produce chlorine, the chlorination step being effected using dry chlorine gas to convert the metal sulphides to chlorides and sulphide sulphur to elemental sulphur.

19. A process as claimed in claim 18, in which zinc is removed from a portion of the lead and silver-depleted solution, and the resulting portion is added to the leaching solution in the leaching step.

20. A process as claimed in claim 19, in which the said portion is electrolysed after removal of zinc therefrom to produce chlorine gas, which is passed to the dry chlorination step.

21. A process as claimed in claim 20, in which sodium carbonate is added to precipitate the zinc as zinc carbonate, sodium hydroxide produced in the electrolysis is carbonated to produce sodium carbonate and the sodium carbonate produced is passed to the zinc carbonate precipitation step.

22. A process as claimed in claim 1, substantially as herein described.

23. A process for recovering metals from an ore containing lead, silver, and zinc sulphides, the process being substantially as herein described with reference to the accompanying drawing.

24. Lead, silver or zinc values when recovered by a process as claimed in any of the preceding claims.

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1516127 COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of the Original on a reduced scale

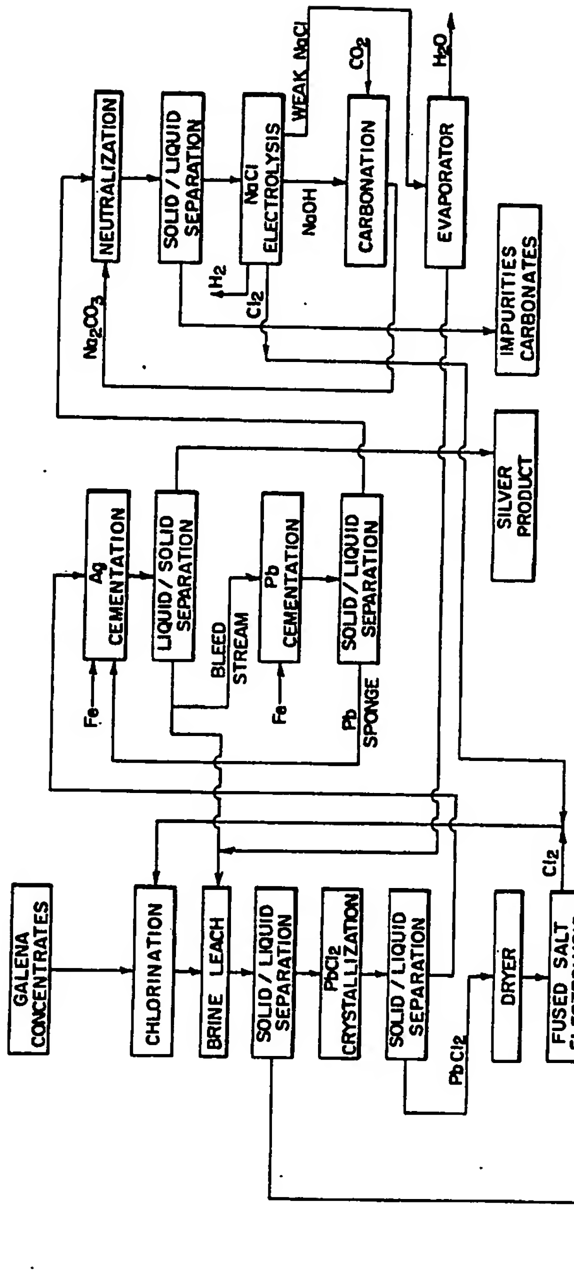

FIG. 1

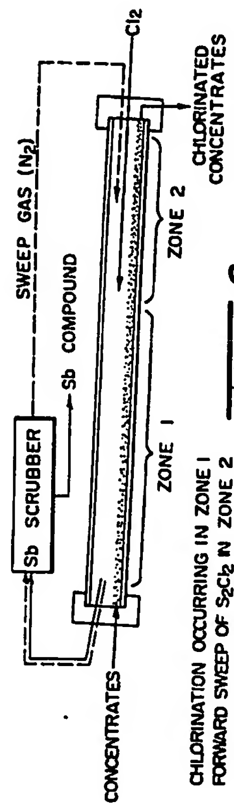

FIG. 2